

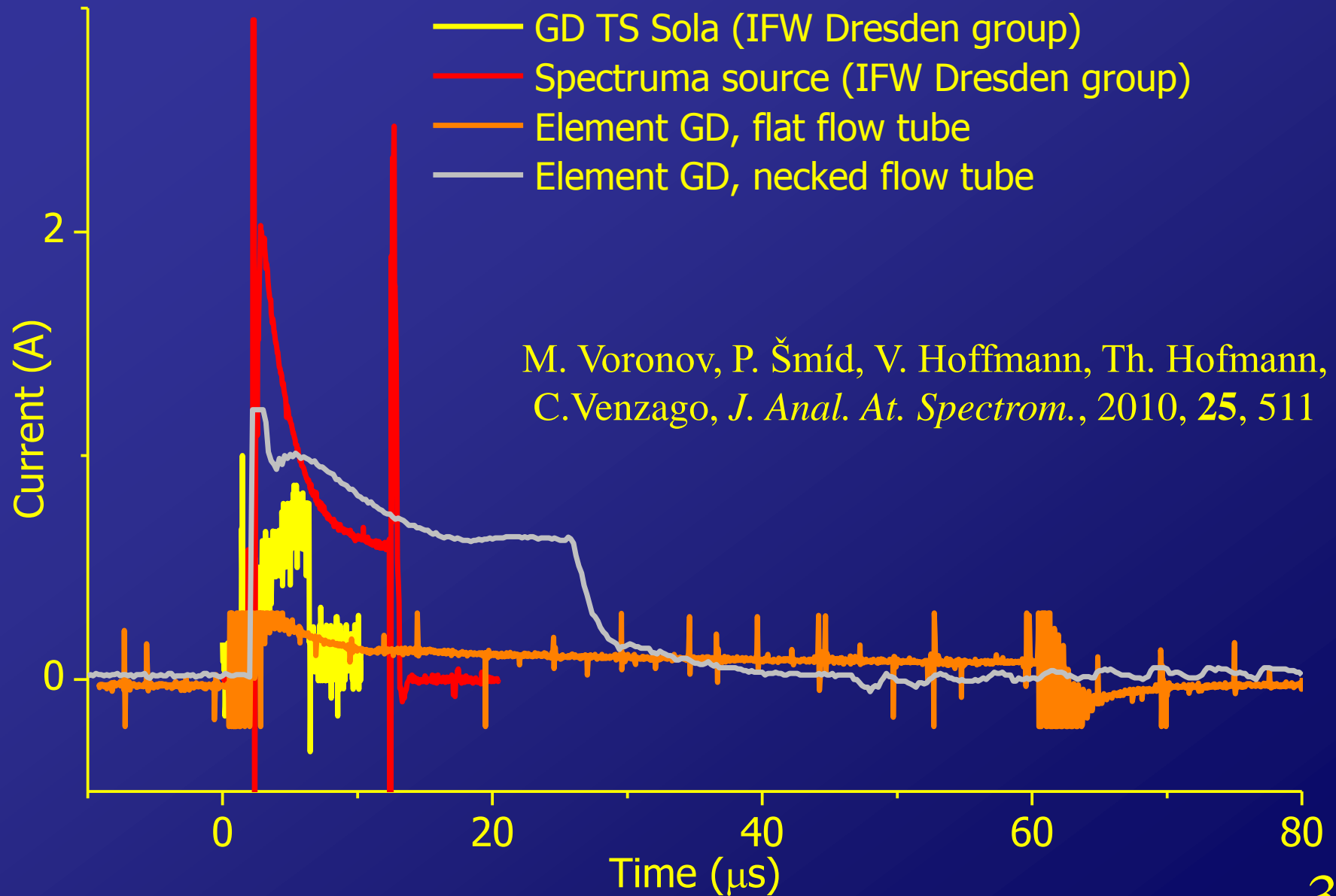
Microsecond Pulsed Glow Discharge Spectrometry

M. Voronov, V. Hoffmann
IFW Dresden

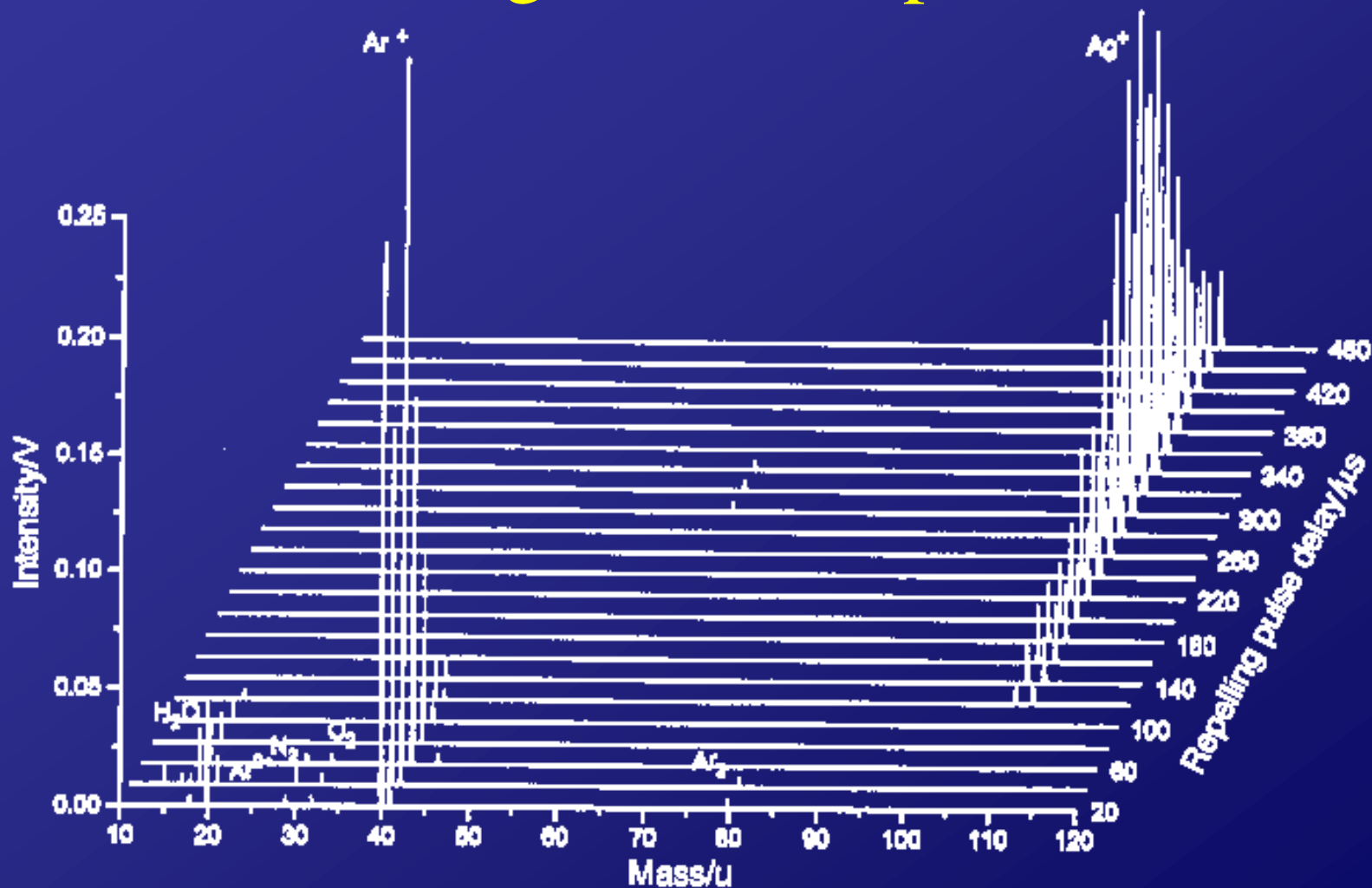
16. Deutsches Anwendertreffen
„Analytische Glimmentladungs-Spektrometrie“
24.-25. April 2013
Duisburg

- PGD applications
- Electrical current prepeak
- Plasma emission prepeak

PGD applications



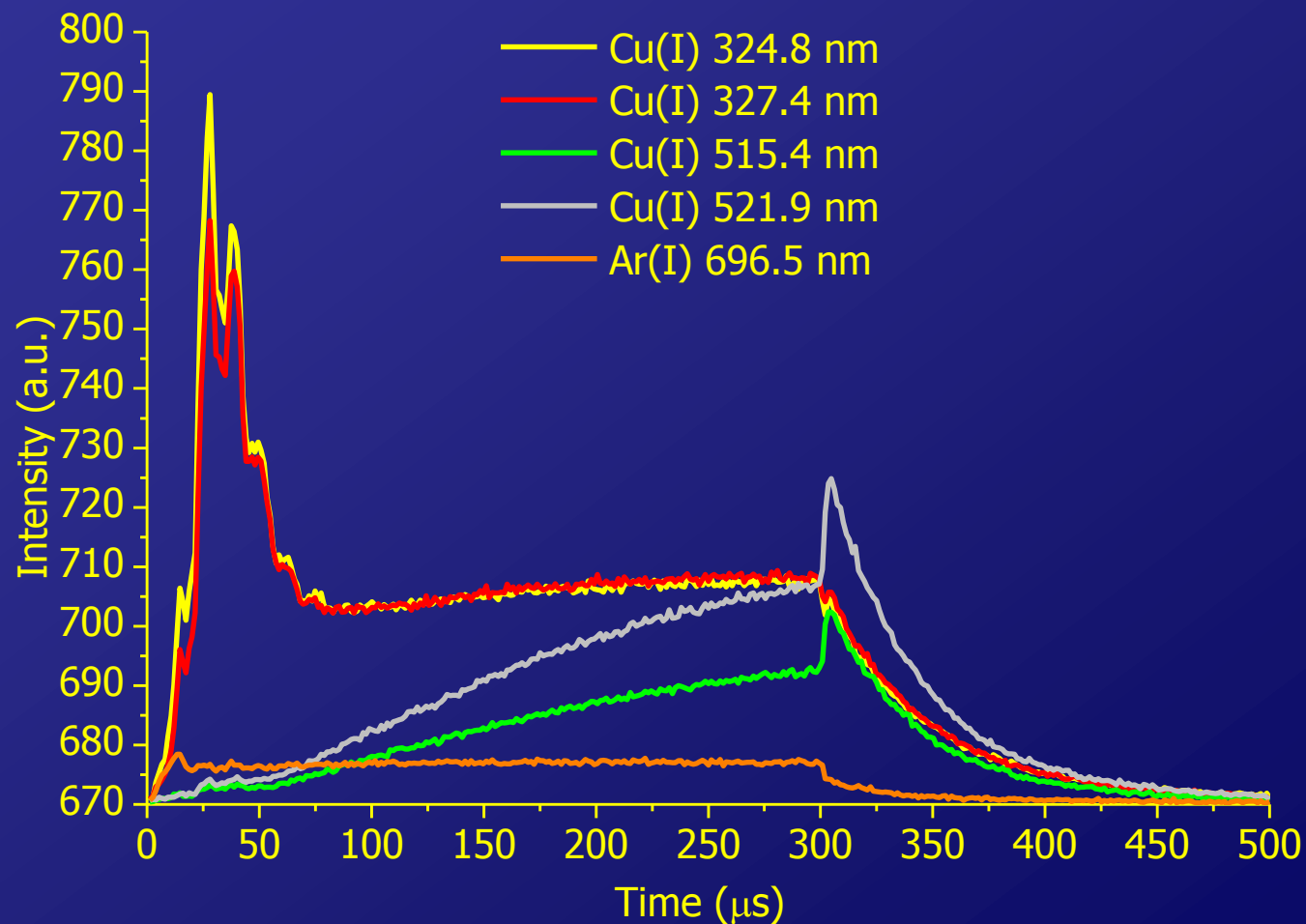
MS: afterglow and separation



W.W. Harrison, W. Hang, X. Yan, K. Ingeneri, C. Schilling,
J. Anal. At. Spectrom., 1997, **12**, 893

Radiation prepeak and afterpeak

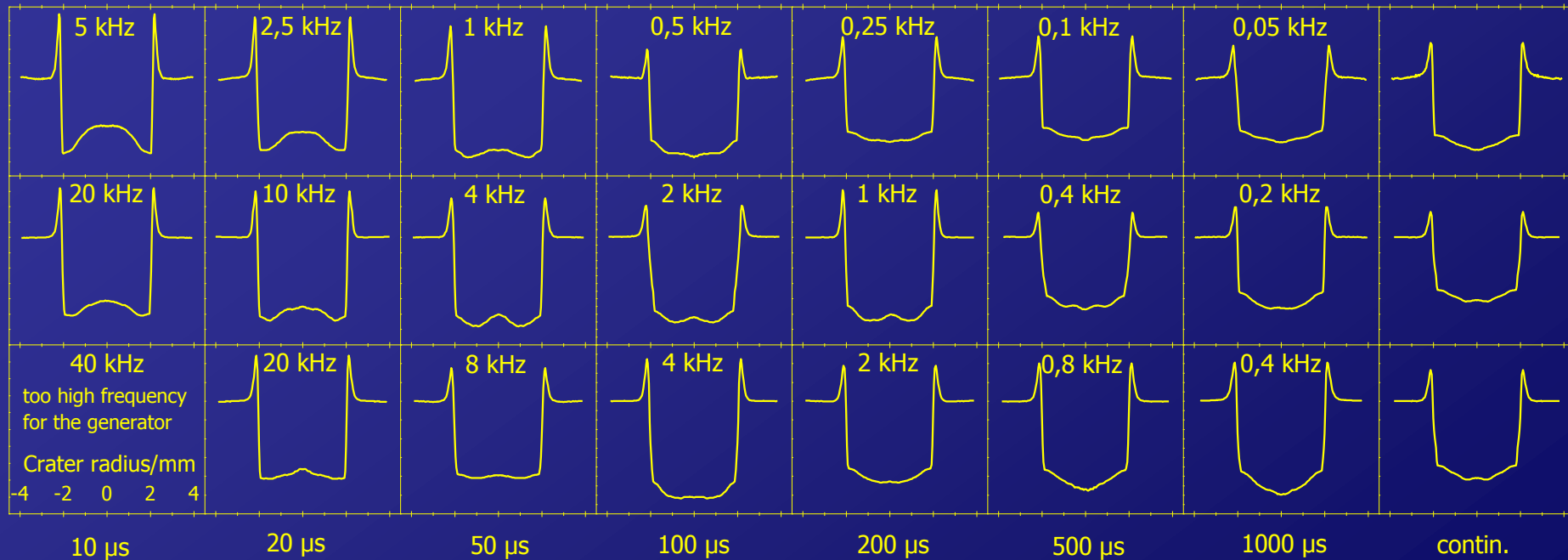
8-mm Grimm
type source
rf 2.24 MHz
 $\tau=300 \mu\text{s}$
 $F=350 \text{ Hz}$
 $p=12 \text{ hPa}$



M. Voronov, V. Hoffmann, T. Wallendorf, S. Marke, J. Mönch, C. Engelhard, W. Buscher, S.J. Ray, G.M. Hieftje, *J. Anal. At. Spectrom.*, 2012, **27**, 419

PGD applications

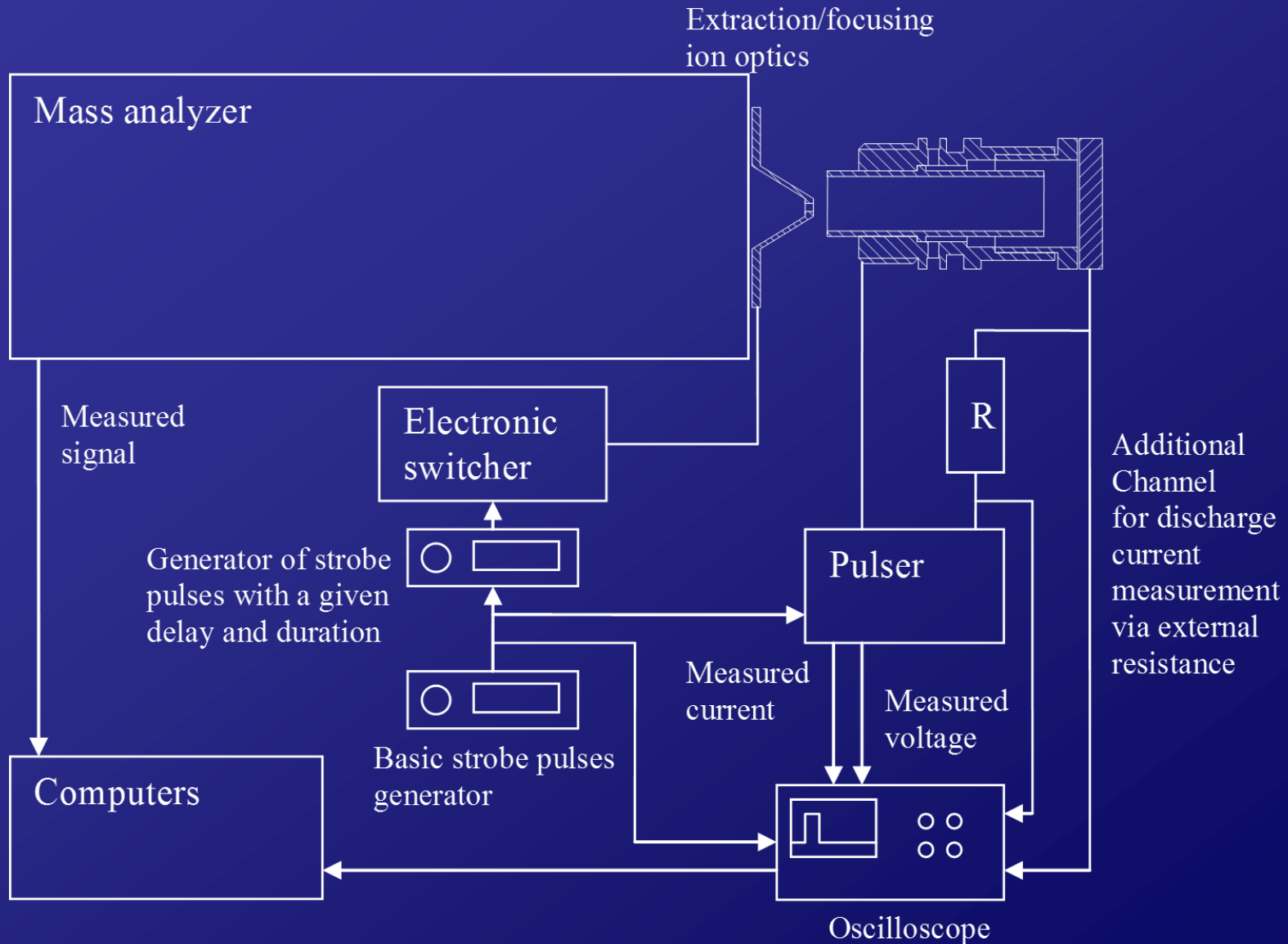
Shapes of craters in Cu samples sputtered with pulsed dc discharge at three different duty cycles (0.05, 0.2 and 0.4) and various pulse lengths (10–1000 μs) (800 V, 7 hPa).



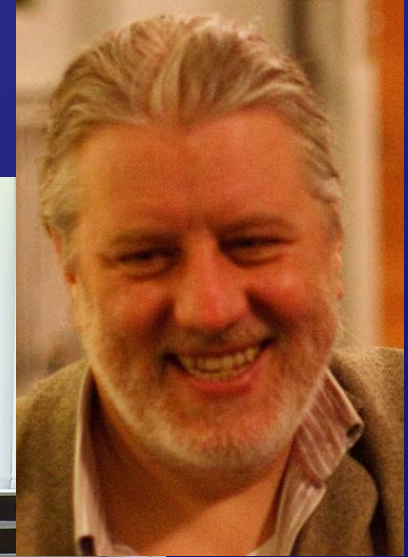
V. Efimova, V. Hoffmann, J. Eckert, *Spectrochimica Acte part B*, 2012, **76**, 181

PGD applications: commercial applications

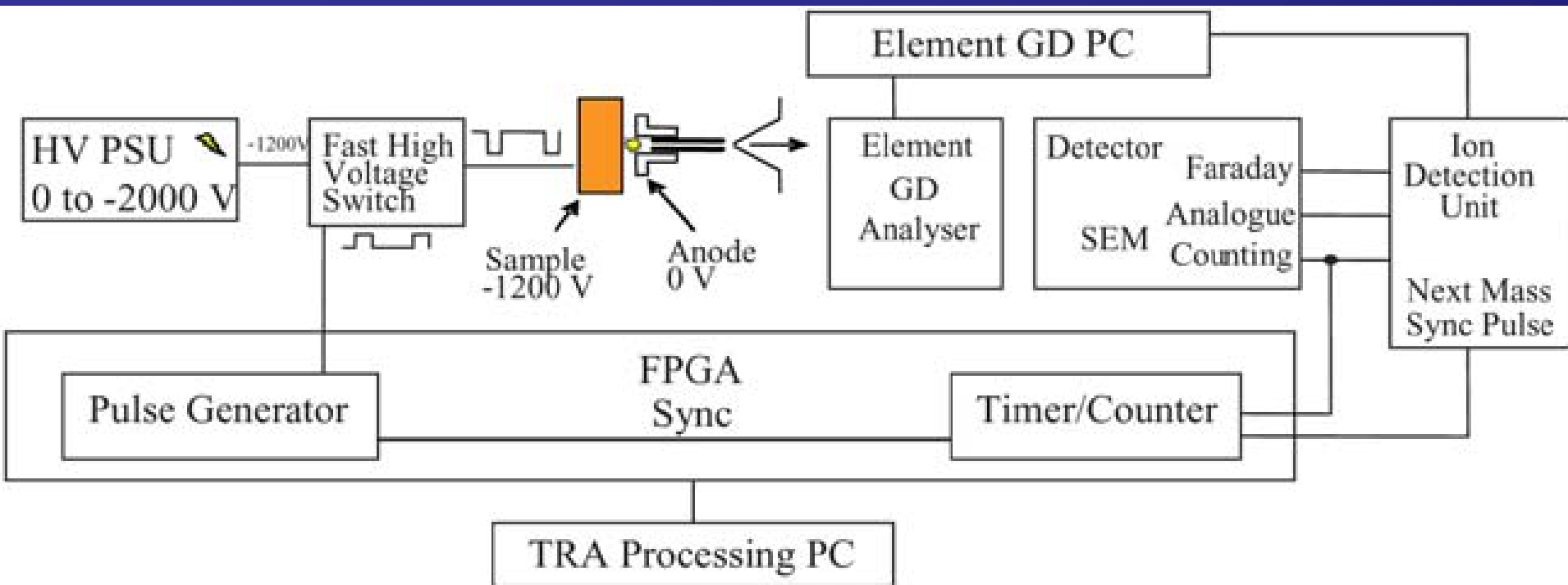
M. Voronov, P. Šmíd, V. Hoffmann, Th. Hofmann, C. Venzago,
J. Anal. At. Spectrom., 2010, **25**, 511



PGD applications: commercial applications



PGD applications: commercial applications

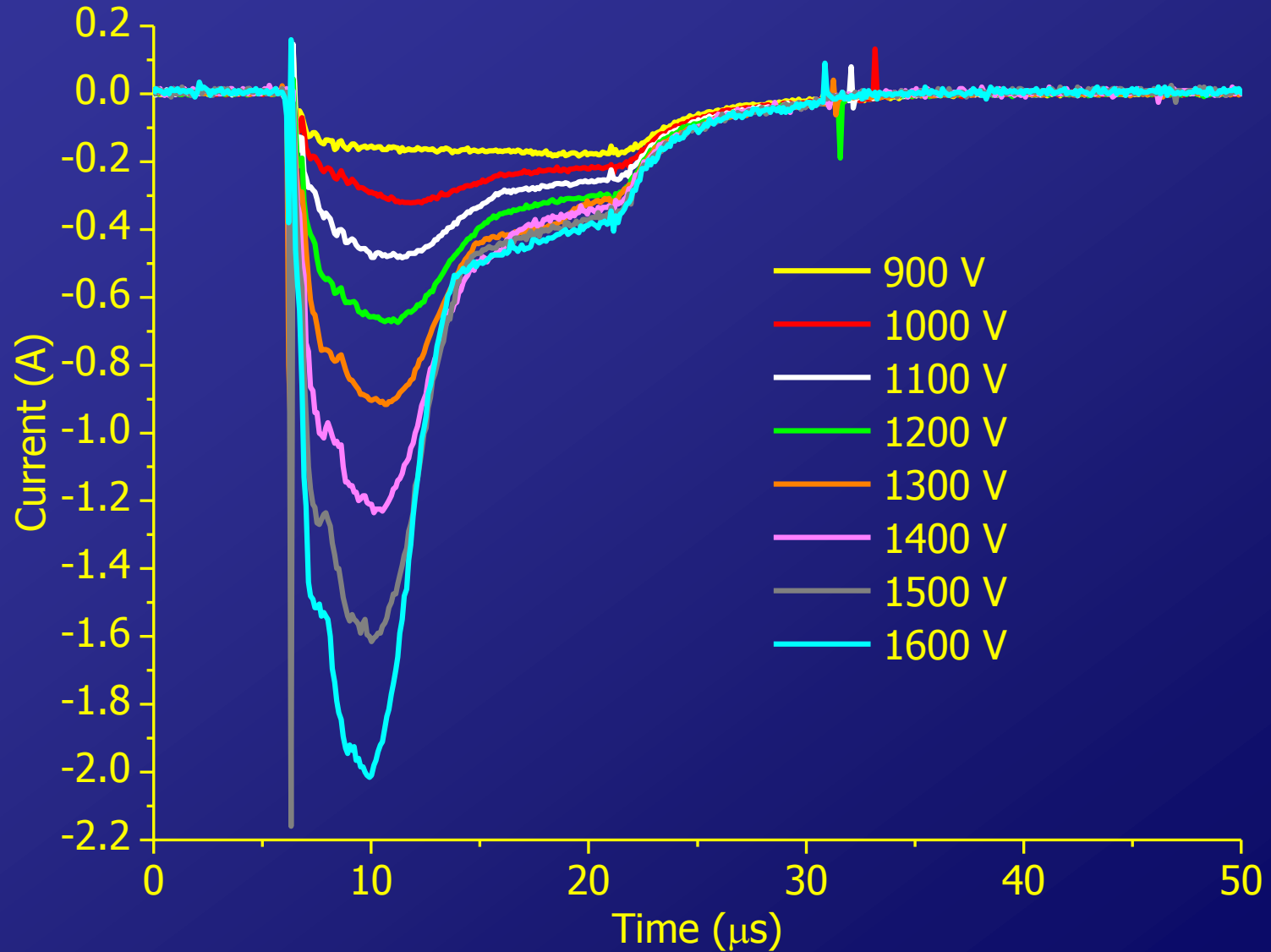


G. Churchill, K. Putyera, V. Weinstein, X. Wang, E.B.M. Steers,
J. Anal. At. Spectrom., 2011, **26**, 2263

- PGD applications
- Electrical current prepeak
- Plasma emission prepeak

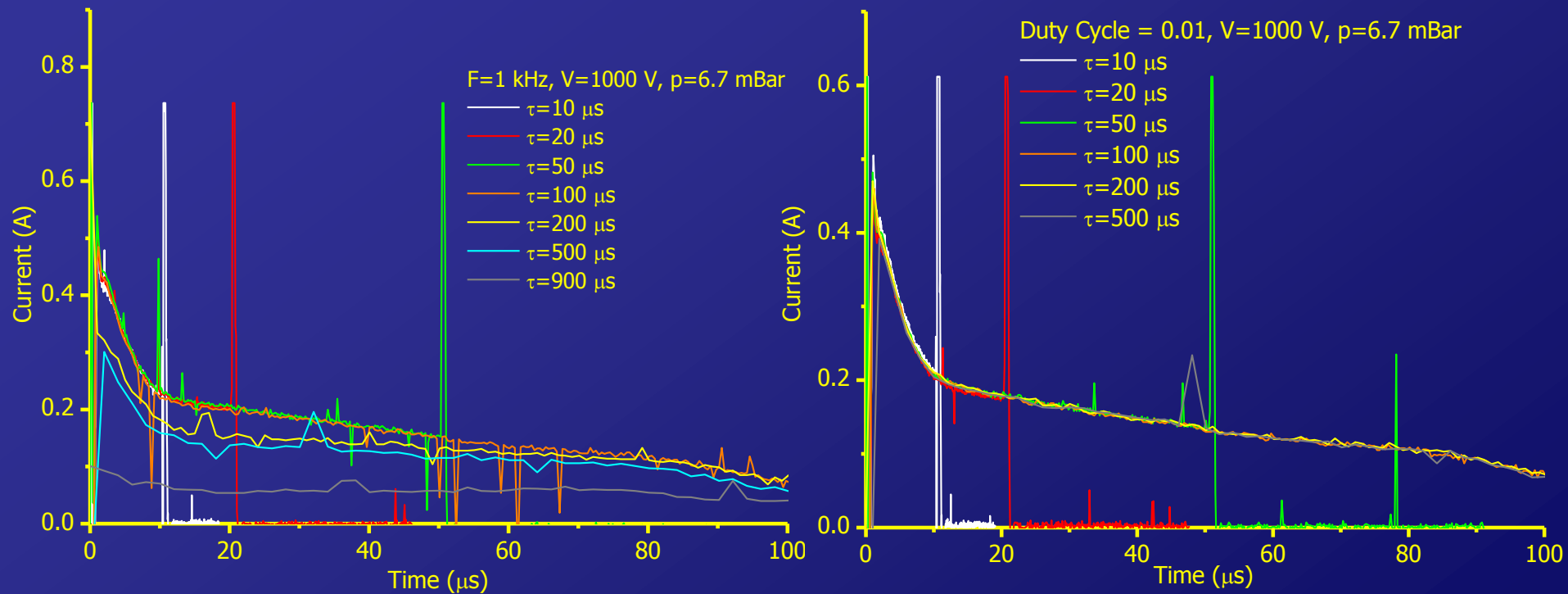
Electrical current prepeak

Modified fast flow Grimm type source. Ar flow = 75 sccm, $p = 2.5$ hPa.



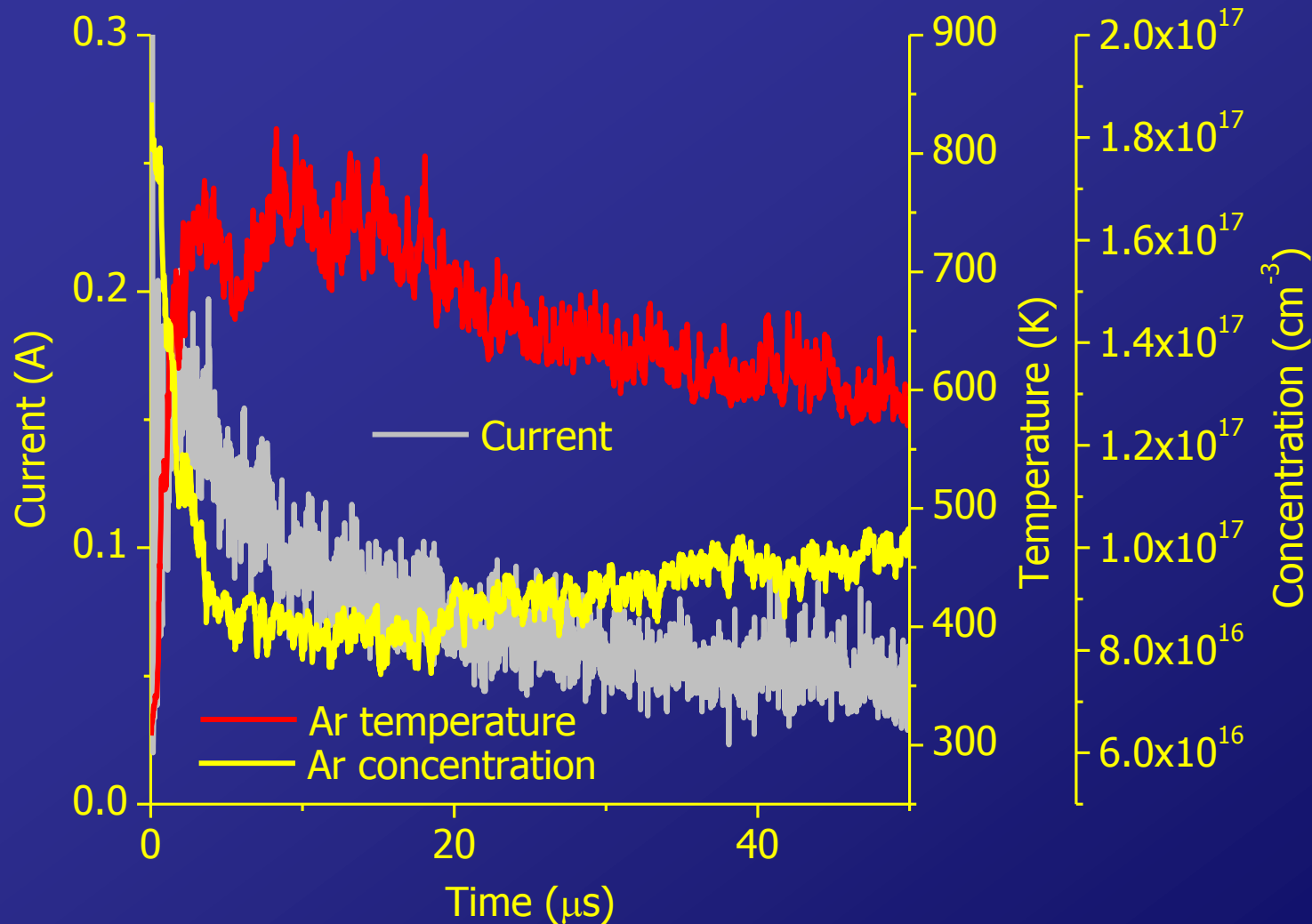
Electrical current prepeak

8-mm Grimm type source, $U=1000$ V, $p=6.7$ hPa.



V. Hoffmann, V.V. Efimova, M.V. Voronov, P. Smid, E.B.M. Steers, J. Eckert,
Journal of Physics: Conference Series, 2008, **133**, 012017

Electrical current prepeak: modelling results

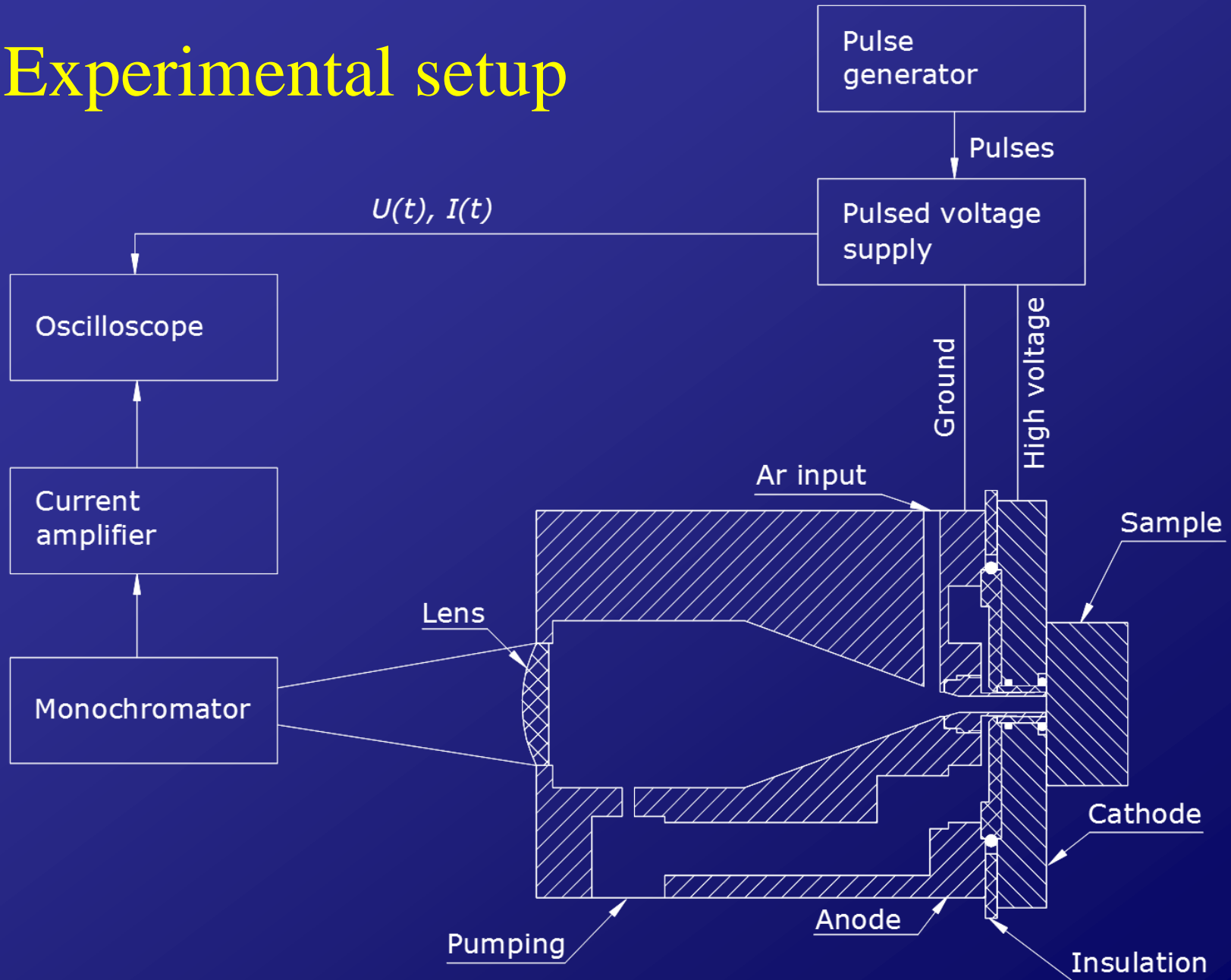


4-mm Grimm
type source,
 $U=1500$ V,
 $p=8$ hPa.

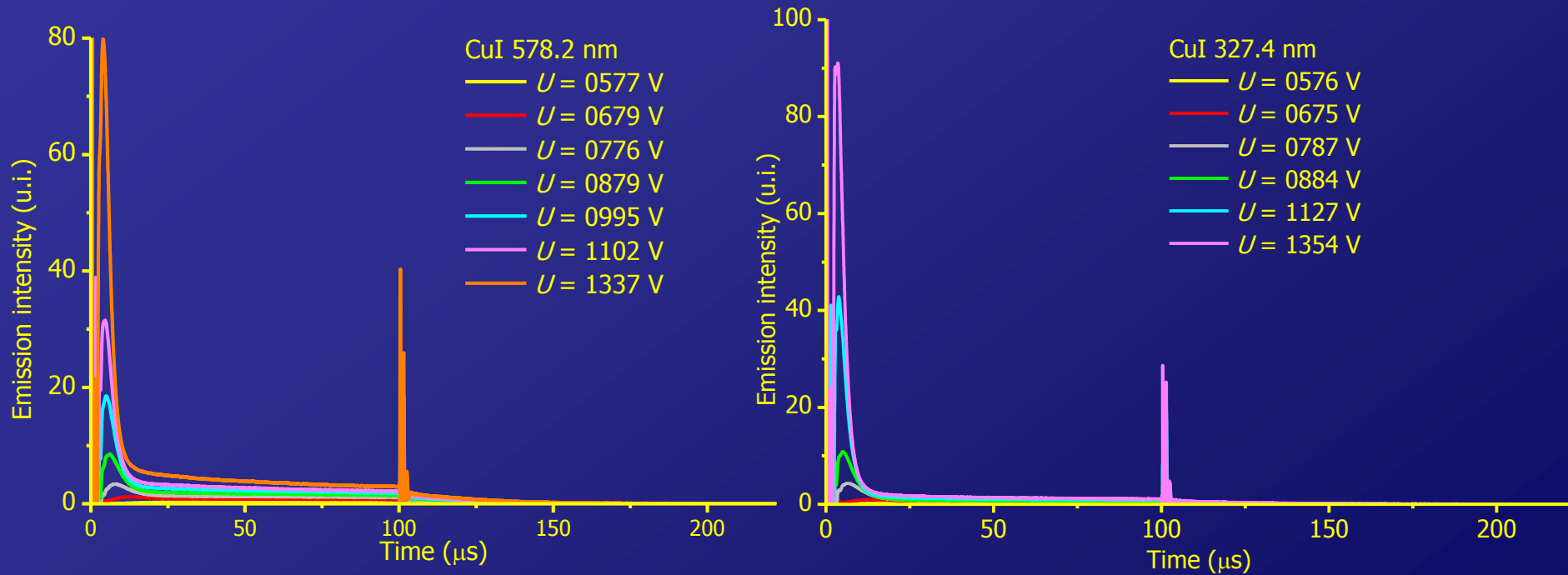
M. Voronov, V. Hoffmann, W. Buscher, C. Engelhard, S.J. Ray, G.M. Hieftje,
J. Anal. At. Spectrom., 2012, **27**, 1225

- PGD applications
- Electrical current prepeak
- Plasma emission prepeak

Experimental setup

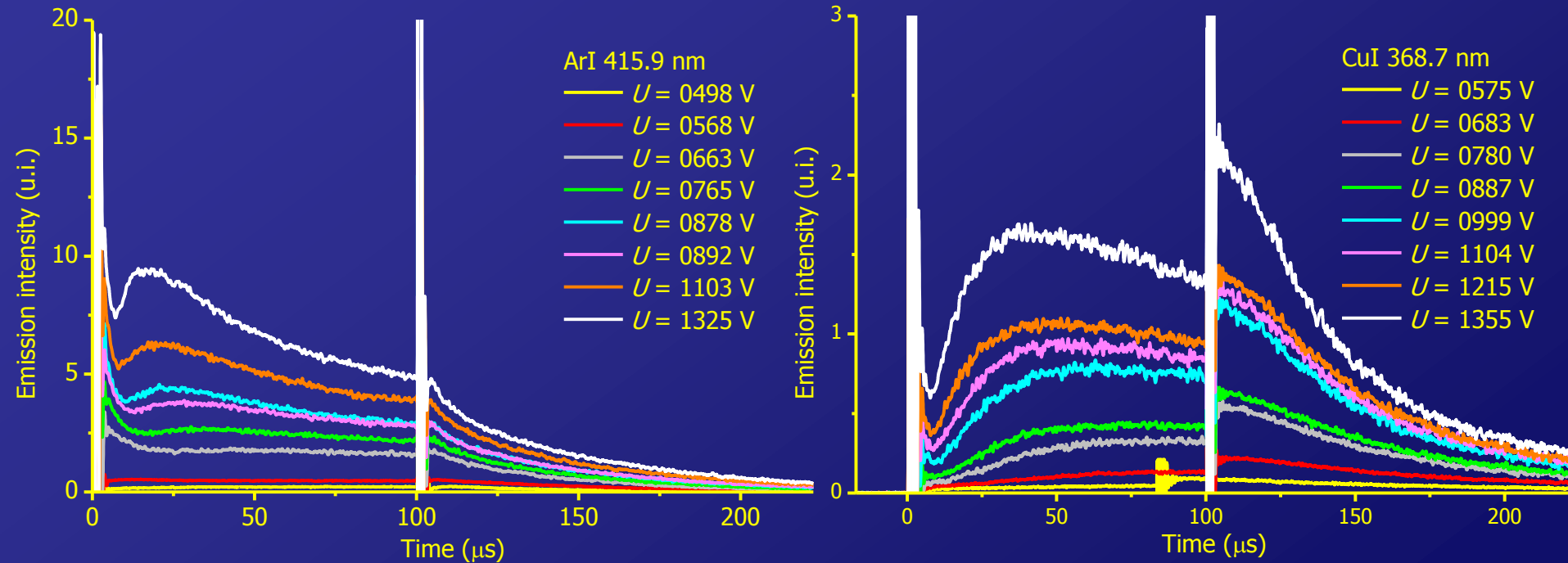


Strong prepeak



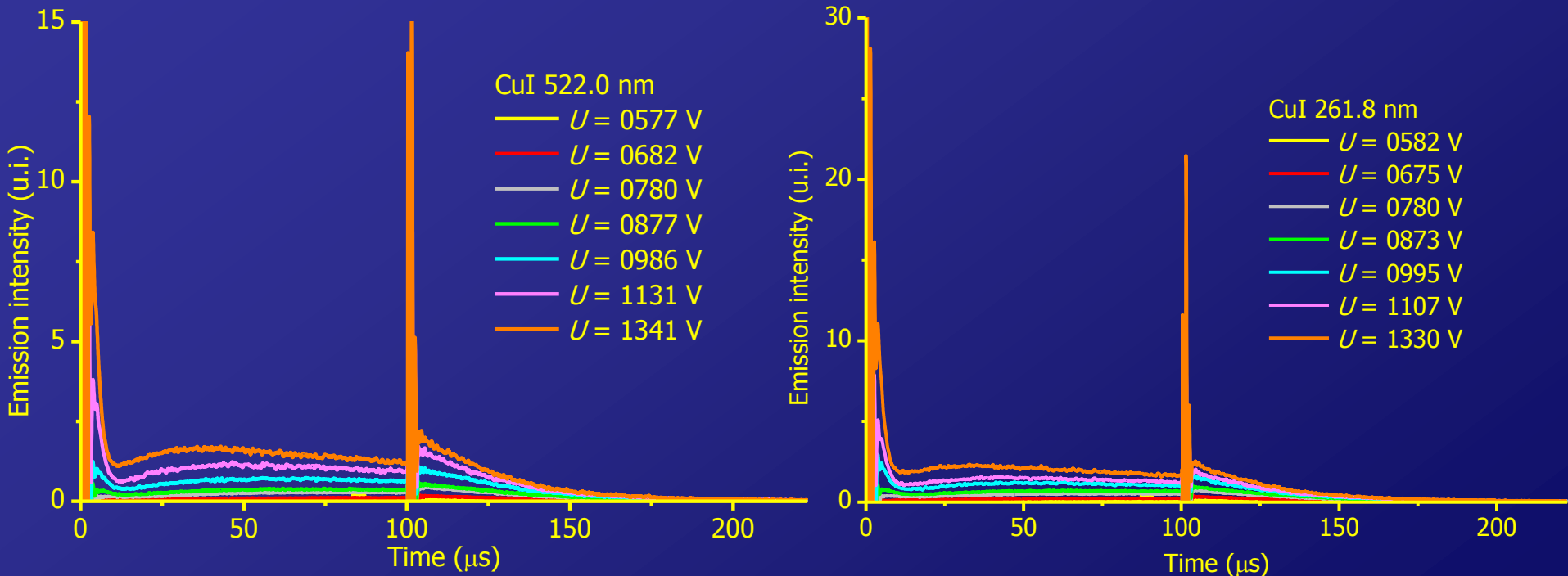
4-mm Grimm type source, $p=6$ hPa, $\tau=100$ μ s, $F=200$ Hz

2 prepeaks



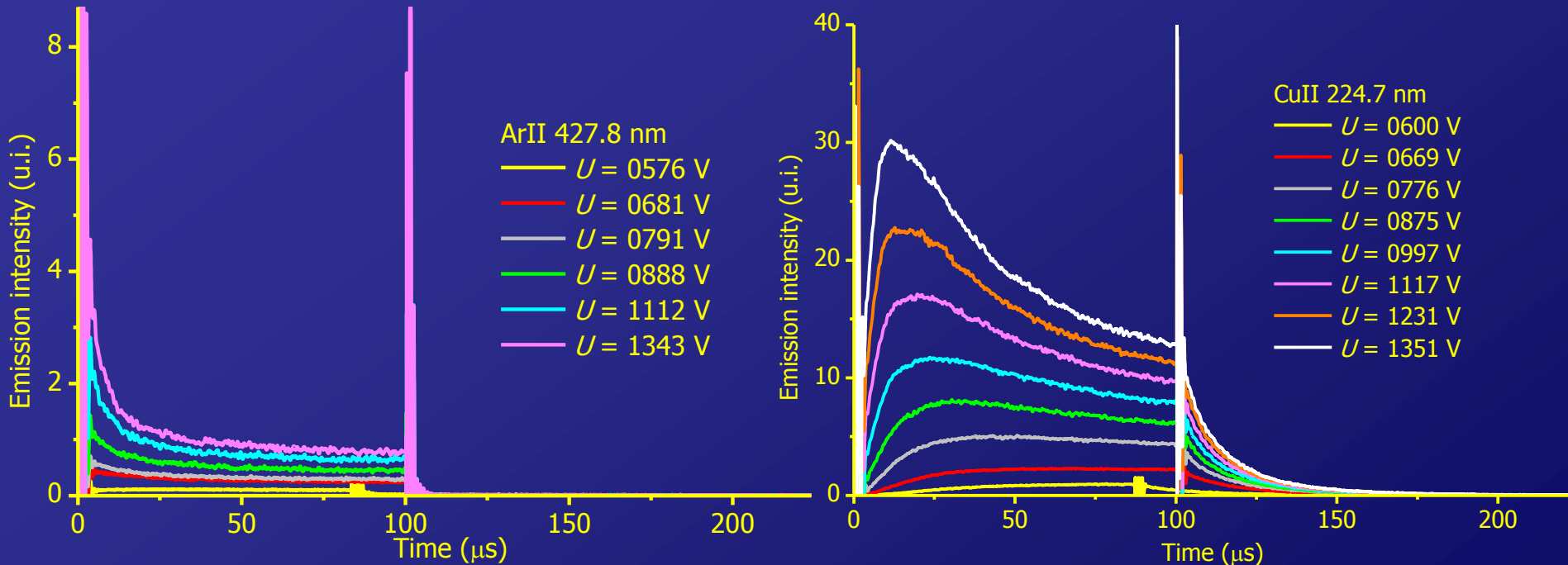
4-mm Grimm type source, $p=6$ hPa, $\tau=100$ μs , $F=200$ Hz

2 prepeaks, the 1st one is strong



4-mm Grimm type source, $p=6$ hPa, $\tau=100$ μs, $F=200$ Hz

Moderate prepeak



4-mm Grimm type source, $p=6$ hPa, $\tau=100 \mu\text{s}$, $F=200$ Hz

Plasma emission prepeak

Line	Lower level energy (eV)	Upper level energy (eV)	Lower state	Upper state
Ar I 415.9	11.55	14.53	$3p^5 ({}^2P_{3/2}) 4s {}^2[3/2]_2^0$	$3p^5 ({}^2P_{3/2}^0) 5p {}^2[3/2]_2$
Ar I 420.1	11.55	14.50	$3p^5 ({}^2P_{3/2}) 4s {}^2[3/2]_2^0$	$3p^5 ({}^2P_{3/2}^0) 5p {}^2[5/2]_3$
Ar I 603.2	13.08	15.13	$3p_5 ({}^2P_{3/2}) 4p {}^2[5/2]_3$	$3p^5 ({}^2P_{3/2}^0) 5d {}^2[7/2]_4^0$
Ar I 696.5	11.55	13.33	$3p^5 ({}^2P_{3/2}) 4s {}^2[3/2]_2^0$	$3p^5 ({}^2P_{1/2}^0) 4p {}^2[1/2]_1$
Cu I 249.2	0	4.97	$3d^{10} ({}^1S) 4s {}^2S_{1/2}$	$3d^9 ({}^2D) 4s4p ({}^3P^0) {}^4P_{3/2}^0$
Cu I 261.8	1.39	6.12	$3d^9 4s^2 {}^2D_{5/2}$	$3d^{10} ({}^1S) 5p {}^2P_{3/2}^0$
Cu I 282.4	1.39	5.78	$3d^9 4s^2 {}^2D_{5/2}$	$3d^9 ({}^2D) 4s4p ({}^3P^0) {}^2D_{5/2}^0$
Cu I 296.1	1.39	5.57	$3d^9 4s^2 {}^2D_{5/2}$	$3d^9 ({}^2D) 4s4p ({}^3P^0) {}^2F_{7/2}^0$
Cu I 324.7	0	3.82	$3d^{10} ({}^1S) 4s {}^2S_{1/2}$	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$
Cu I 327.4	0	3.79	$3d^{10} ({}^1S) 4s {}^2S_{1/2}$	$3d^{10} ({}^1S) 4p {}^2P_{1/2}^0$
Cu I 368.7	3.82	7.18	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$	$3d^{10} ({}^1S) 6d {}^2D_{5/2}$
Cu I 465.1	5.07	7.74	$3d^9 ({}^2D) 4s4p ({}^3P^0) {}^4F_{9/2}^0$	$3d^9 4s ({}^3D) 5s {}^4D_{7/2}$
Cu I 510.6	1.39	3.82	$3d^9 4s^2 {}^2D_{5/2}$	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$
Cu I 515.3	3.79	6.19	$3d^{10} ({}^1S) 4p {}^2P_{1/2}^0$	$3d^{10} ({}^1S) 4d {}^2D_{3/2}$
Cu I 521.8	3.82	6.19	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$	$3d^{10} ({}^1S) 4d {}^2D_{5/2}$
Cu I 522.0	3.82	6.19	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$	$3d^{10} ({}^1S) 4d {}^2D_{3/2}$
Cu I 570.0	1.64	3.82	$3d^9 4s^2 {}^2D_{3/2}$	$3d^{10} ({}^1S) 4p {}^2P_{3/2}^0$
Cu I 578.2	1.64	3.79	$3d^9 4s^2 {}^2D_{3/2}$	$3d^{10} ({}^1S) 4p {}^2P_{1/2}^0$
Ar II 294.3	17.14	21.35	$3s^2 3p^4 ({}^3P) 4s {}^2P_{3/2}$	$3s^2 3p^4 ({}^1D) 4p {}^2P_{3/2}^0$
Ar II 329.4	19.87	23.63	$3s^2 3p^4 ({}^3P) 4p {}^2P_{3/2}^0$	$3s^2 3p^4 ({}^3P) 4d {}^2P_{3/2}$
Ar II 378.1	19.49	22.77	$3s^2 3p^4 ({}^3P) 4p {}^4D_{7/2}^0$	$3s^2 3p^4 ({}^3P) 4d {}^4D_{7/2}$
Ar II 427.8	18.45	21.35	$3s^2 3p^4 ({}^1D) 4s {}^2D_{5/2}$	$3s^2 3p^4 ({}^1D) 4p {}^2P_{3/2}^0$
Ar II 434.8	16.64	19.49	$3s^2 3p^4 ({}^3P) 4s {}^4P_{5/2}$	$3s^2 3p^4 ({}^3P) 4p {}^4D_{7/2}^0$
Ar II 461.0	18.45	21.14	$3s^2 3p^4 ({}^1D) 4s {}^2D_{5/2}$	$3s^2 3p^4 ({}^1D) 4p {}^2F_{7/2}^0$
Ar II 611.5	19.12	21.14	$3s^2 3p^4 ({}^1D) 3d {}^2G_{9/2}$	$3s^2 3p^4 ({}^1D) 4p {}^2F_{7/2}^0$
Cu II 224.7	2.72	8.23	$3d^9 ({}^2D) 4s {}^3D_3$	$3d^9 ({}^2D) 4p {}^3P_2^0$

Strong prepeak

2 prepeaks

2 prepeaks, the 1st

one is strong

Moderate prepeak

Summary

- PGD can enhance detected analytical signal and reduce thermal stress of the sample
- Electrical current prepeak is generated by Ar heating and expansion at the leading edge of the discharge
- Plasma emission prepeak exists at all detected lines at high voltage. Profile of the prepeak depends on the transition